

Docket No.: 14113-00003-US
(PATENT)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of:
Philipp Stoessel et al.

Application No.: 10/578,039

Confirmation No.: 5478

Filed: May 1, 2006

Art Unit: 1625

For: METAL COMPLEXES WITH BIPODAL
LIGANDS

Examiner: C. Aulakh

1.132 DECLARATION

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

1. I, Dr. Philipp Stoessel, am a citizen of the Federal Republic of Germany and reside at Sophienstrasse 30, 60487 Frankfurt, Germany, hereby declare and say as follows:

2. I am a fully trained chemist, having studied chemistry at the University of Tübingen, Baden-Württemberg, Germany. I am well acquainted with technical English.

3. Work experience:

1986-1996: Studies in chemistry at the University of Tübingen, Germany

1996-1998: Postdoctoral research in chemistry sponsored by the Alexander von Humboldt Foundation with Dr. J. R. Norton at the Colorado State University, Fort Collins, CO and at the Columbia University New York, NY.

1998-1999: Material Scientist and Synthetic Chemist at the Institut für Neue Materialien, Saarbrücken, Saarland, Germany

1999-2005: Material Scientist and Synthetic Chemist at COVION Organic Semiconductors GmbH, Frankfurt, Hessen, Germany.

2005-today: Material Scientist and Synthetic Chemist at the Merck (formerly Merck Organic Materials GmbH, Frankfurt, Hessen, Germany, and today Merck KGaA, Darmstadt, Hessen, Germany).

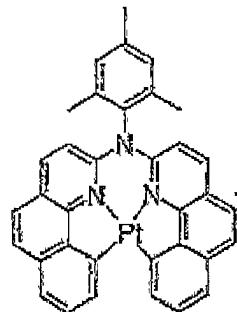
4. In the field of organic light emitting diode (OLED), I am an inventor on more than 70 U.S. patents and patent applications and an author of more than 10 publications and lectures.

5. In view of my qualifications as outlined above, I consider myself to be an expert and to be skilled in phosphorescent emitters and platinum complexes and in the OLED field.

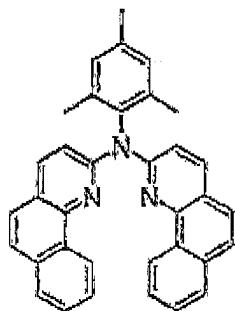
6. I have read and reviewed U. S. Serial No.; 10/578,039 (" '039 application") including the office actions and responses.

7. I had the following experiments conducted under my supervision:

8. Synthesis of Pt-complex of bis(benzo[h]quinolin-2-yl)-(2,4,6-trimethylphenyl)-amine (complex Pt-1)



a) Bis(benzot[h]quinolin-2-yl)-(2,4,6-trimethylphenyl)-amine



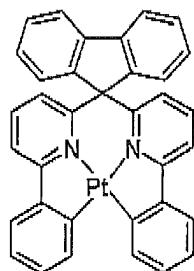
9. In a mixture of 25.8 g (100 mmol) of 2-bromo-phenanthridine [1097204-18-6] and 6.8 g (50 mmol) of 2,4,6-trimethylaniline [88-05-1] in 300 ml of toluene the following was added 11.5 g (120 mol) sodium-tert-butylate, 5 ml (5 mmol) tri-tert-butyl phosphine (1 M solution in toluene) and 561 mg (2.5 mmol) palladium(II)acetate. The reaction mixture was stirred under reflux for 12 hours and was then allowed to cool to 60 °C. Then 500 ml of water was added to the reaction mixture, the organic layer was separated, washed once with 500 ml water, once with 500 ml brine and then dried over magnesium sulphate. The organic phase was filtered through a short pad of silica, the silica was rinsed twice with approximately 200 ml of toluene, and the combined organic phases were concentrated in vacuum. The residual viscous oil was purified twice by re-crystallization from ethyl acetate / ethanol (3:1) and once by fractionated high vacuum sublimation (Temperature approximately 300-320 °C, pressure approximately 10^{-5} mbar). The yield was 15.5 g (32 mmol), 64 %, purity: approximately 99.0 % by $^1\text{H-NMR}$. The results are attached.

10. Pt-complex of bis(benzo[h]quinolin-2-yl)-(2,4,6-trimethylphenyl)-amine (complex Pt-1)

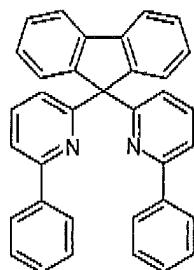
11. A mixture of 12.2 g (25 mmol) bis(benzo[h]quinolin-2-yl)-(2,4,6-trimethylphenyl)-amine and 6.6 g (25 mmol) platinum(II)chloride [10025-65-7] in 150 ml benzonitrile was heated

under reflux for 60 hours. After cooling to room temperature and slow addition of 100 ml methanol the mixture was stirred for 16 hours at room temperature, after which time the brown precipitate formed was filtered off, washed three times with 30 ml methanol each and dried in vacuum. The precipitate was suspended in 150 ml glacial acetic acid, 20 ml pyridine and 5 g zinc dust was added and the mixture was stirred at 70°C for 16 hours. The mixture was allowed to cool to room temperature, the orange solid was filtered off, washed once with 30 ml acetic acid, three times with 30 ml water/ethanol (1:1, v/v), three times with ethanol and dried in vacuum. The orange solid was placed in a hot steam extractor and extracted with toluene (approximatley 250 ml in the receiver) through a pad of alumina (basic, activity stage 1). After approximately 60 hours the orange microcrystalline product was filtered off, washed with ethanol and dried in vacuum. The hot steam extraction process was repeated 3 more times. The orange microcrystalline product was then zone sublimed twice (Temperature approximately. 340-350 °C, pressure approximately 10^{-6} mbar). The yield was 8.9 g (13 μmol), 52 %, purity: approximately 99.9 % by HPLC. The results are attached.

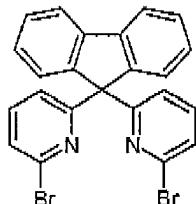
12. Synthesis of Pt-complex of 9,9-Bis(6-phenyl-pyridin-2-yl)fluorene (complex Pt-2)



Synthesis of ligand 9,9-Bis(6-phenyl-pyridin-2-yl)fluorene



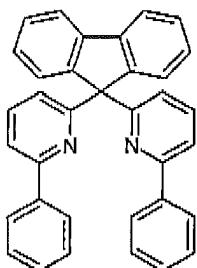
13. 9,9-Bis(6-bromo-pyridin-2-yl)fluorene



14. A Grignard-reagent was prepared in the usual manner from 15.5 g (590 mmol) magnesium turnings, activated by dry stirring with a small crystal of iodine for 30 min, and 147.6 g (633 mmol) 2-bromo-biphenyl, dissolved in a mixture of 800 ml THF, 400 ml toluene, 100 ml 1,2-dimethoxyethane and 5.0 ml 1,2-dibromoethane. After complete addition of the 2-bromo-biphenyl solution to the magnesium the mixture was stirred under reflux until all the magnesium has reacted (app. 2 h). The Grignard reagent was allowed to cool to room temperature and then treated dropwise with a solution of 194.7 g (569 mmol) of di(6-bromo-2-pyridyl)ketone in 1200 ml of THF. When the exothermic reaction subsided, the mixture was heated under reflux for another 2 h. Then the THF was completely removed under reduced pressure (10 mbar), the residual foam was re-dissolved in 2000 ml acetic acid at 60 °C, then 130 ml of acetic anhydride were added, the mixture was heated under reflux and then carefully

treated dropwise with a mixture of 100 ml of concentrated sulphuric acid and 100 ml of acetic acid (Caution: exothermic reaction!). When the exothermic reaction subsided, the mixture was heated under reflux for another 1 h. The reaction mixture was allowed to cool to room temperature and then carefully added to 3 kg of crushed ice. The mixture was made alkaline by addition of a solution of 400 g NaOH in 1000 ml of water and then extracted with four 500 ml portions of dichloromethane. The combined organic phases were washed once with 500 ml of brine and then dried over magnesium sulphate. The organic phase was reduced in volume by distilling the dichloromethane off until the crystallisation of the product started (app. 400 ml), at which point 1000 ml of ethanol were slowly added. The pale green crystals were collected by suction filtration, washed with three portions of app. 150 ml ethanol each and finally dried in vacuum. Yield: 161.2 g (337 mmol), 59 %, purity: app. 98 % by $^1\text{H-NMR}$.

15. 9,9-Bis(6-phenyl-pyridin-2-yl)fluorene

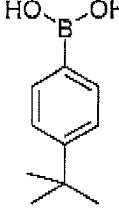
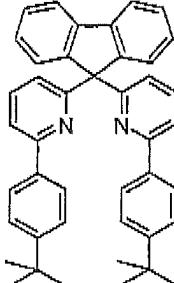


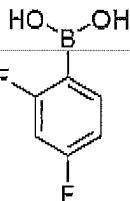
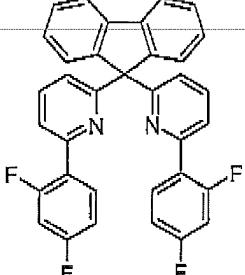
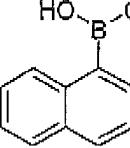
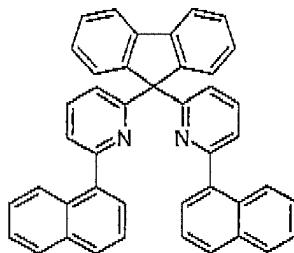
16. To a mixture of 95.6 g (200 mmol) of 9,9-bis(6-bromo-pyridin-2-yl)fluorene, 97.5 g (800 mmol) of benzene boronic acid and 72.0 g (1.24 mol) of anhydrous potassium fluoride in 1000 ml of THF were added 1.8 g (8.7 mmol) of tri-tert-butyl phosphine and then 1.5 g (6.6 mmol) of palladium(II)acetate. The reaction mixture was stirred under reflux for 7 h and

then - while still being hot - treated dropwise with a mixture of 1000 ml of water and 1000 ml of ethanol. The grey precipitate formed was filtered off and successively washed three times with app. 300 ml of a water/ethanol mixture (1:1 vv), then three times with app. 200 ml of ethanol each and then dried in vacuum. The raw product was placed in a hot steam extractor and extracted with chloroform through a pad of silica. The suspension was reduced in volume to app. 300 ml in vacuum at which point 1000 ml of EtOH were slowly added. The colourless crystals were collected by suction filtration, washed with three portions of app. 150 ml ethanol each, dried in vacuum and then sublimed in high vacuum ($T = 300 \text{ }^{\circ}\text{C}$, p app. 10^{-5} mbar), in order to eliminate traces of palladium. Yield: 82.6 g (175 mmol), 87 %, purity: app. 99.5 % by $^1\text{H-NMR}$.

17. By using the same method as described above the ligands shown in table 1, were prepared from the corresponding boronic acids:

18. Table 1:

boronic acid	ligand	yield
		64 %

		88 %
		82 %

19. Pt-complex of 9,9-Bis(6-phenyl-pyridin-2-yl)fluorene (complex Pt-2)
20. A suspension of 25.0 g (53 mmol) of 9,9-bis(6-phenyl-pyridin-2-yl)fluorene, 22.0 g (53 mmol) potassium tetrachloroplatinate and 160.0 g (2.4 mol) lithium acetate in 1500 ml anhydrous acetic acid was heated under reflux for 60 h. The reaction mixture was allowed to cool to room temperature, the acetic acid was removed in vacuum, the residue was suspended in 500 ml of ethanol, filtered off, washed five times with 100 ml of ethanol each and then dried in vacuum. The raw product was placed in a hot steam extractor and extracted with chloroform through a pad of silica. After app. 60 h the suspension formed was reduced in volume to app. 200 ml in vacuum at which point 500 ml of ethanol were slowly added. The yellow microcrystalline product was filtered off, washed with ethanol, dried in vacuum and then re-crystallized twice

from boiling DMF (app. 130 ml / g). The yellow crystals were zone sublimed twice ($T = 340 - 350^{\circ}\text{C}$, p app. 10^{-5} mbar). Yield: 8.6 g (13 mmol), 24 %, purity: app. 99.9 % by HPLC.

21. By using the same method as described for complex Pt-2 the complexes shown in table 2, were prepared from the corresponding ligands.

22. Table 2:

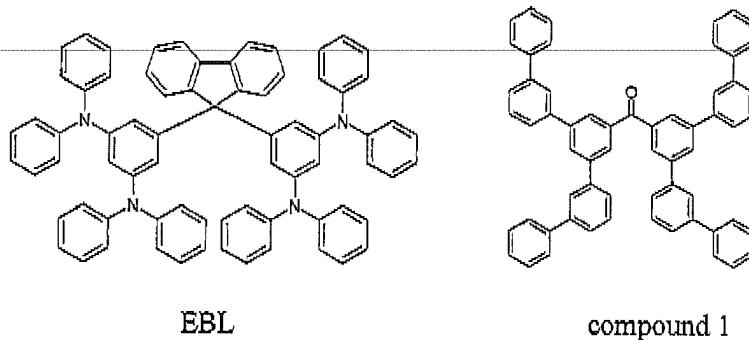
complex	ligand	complex	yield
Pt-3			46 %
Pt-4			25 %
Pt-5			16 %

23. Production and characterisation of organic electroluminescent devices
24. Electroluminescent devices according to the invention were produced as described, for example, in WO 2005/003253. The results for various OLEDs are given here. The basic structure, the materials used, the degree of doping and the layer thicknesses thereof are identical for better comparability.

25. Device Structure

Hole-injection layer (HIL)	20 nm of 2,2',7,7'-tetrakis(di-para-tolylamino)spiro-9,9'-bifluorene
Hole-transport layer (HTL)	20 nm of NPB (N-naphthyl-N-phenyl-4,4'-diaminobiphenyl)
Electron-blocking layer (EBL, optional)	15 nm of EBL (9,9-bis(3,5-diphenylaminophenyl)-fluorene)
Emission layer (EML)	40 nm of host material, compound 1 (see below); dopant: 10% by vol.; complexes Pt-2 or Pt-3
Electron-transport layer (ETL)	20 nm of AlQ ₃ (tris(quinolinato)aluminium(III))
Cathode	1 nm of LiF, 100 nm of Al on top.

26. The following materials were used for the construction of the organic electroluminescent devices:



27. These as yet unoptimised OLEDs were characterised by standard methods; the electroluminescence spectra, the efficiency (measured in cd/A) as a function of the luminance, calculated from current-voltage-luminance characteristic lines (IUL characteristic lines), and the lifetime were determined for this purpose.

28. As evident from Table 3, the electroluminescent devices show good color coordinates, high efficiencies and high lifetime.

29. Table 3: Device results with compounds according to the invention

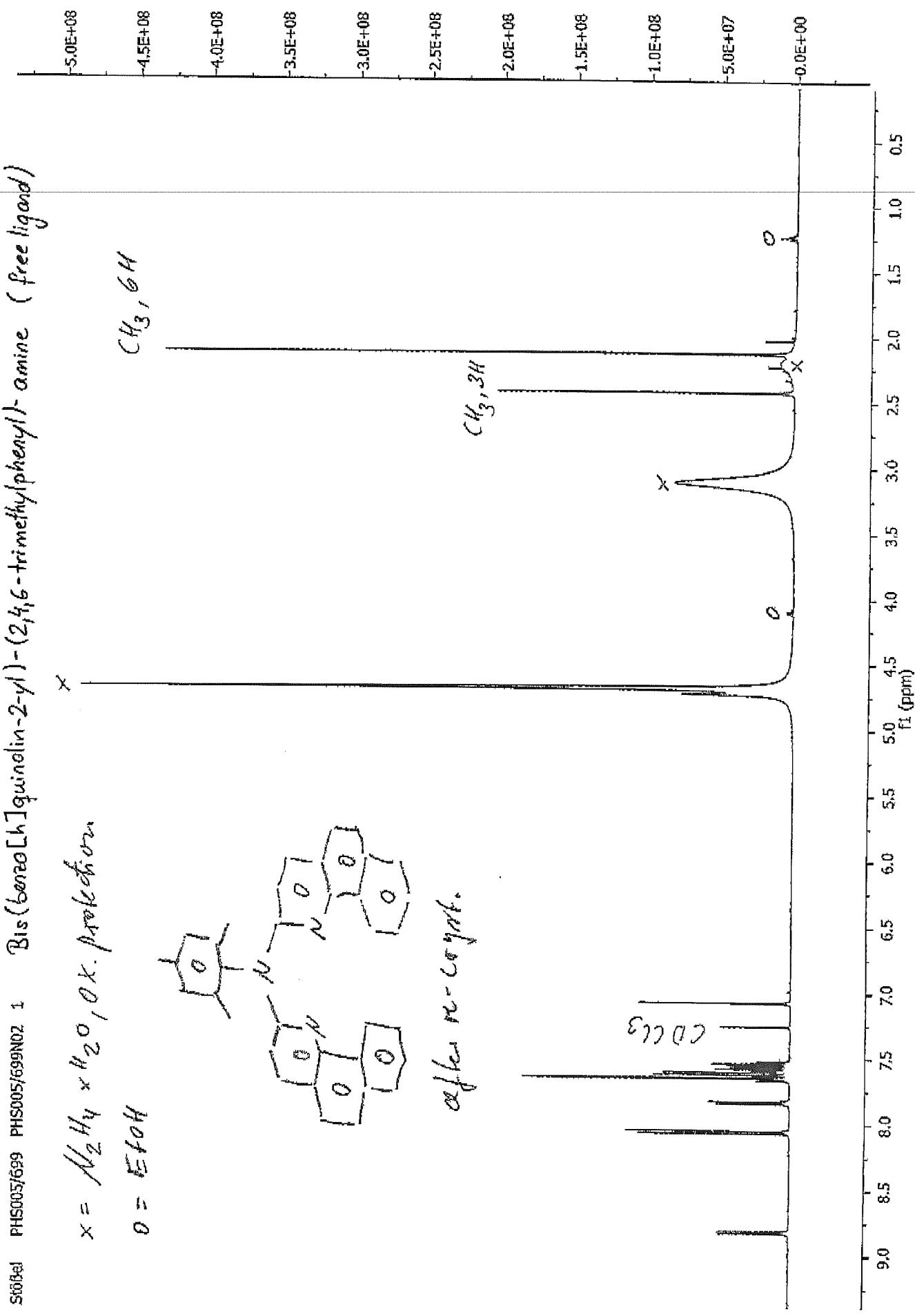
EML	max. Eff. [cd/A]	voltage [V] at 1000 cd/m ²	CIE (x, y)	lifetime [h], starting brightness 1000 cd/m ²
comp. 1 / Pt-2	55.0	5.0	0.34, 0.62	4000
comp. 1 / Pt-3	57.4	5.6	0.34, 0.62	9500

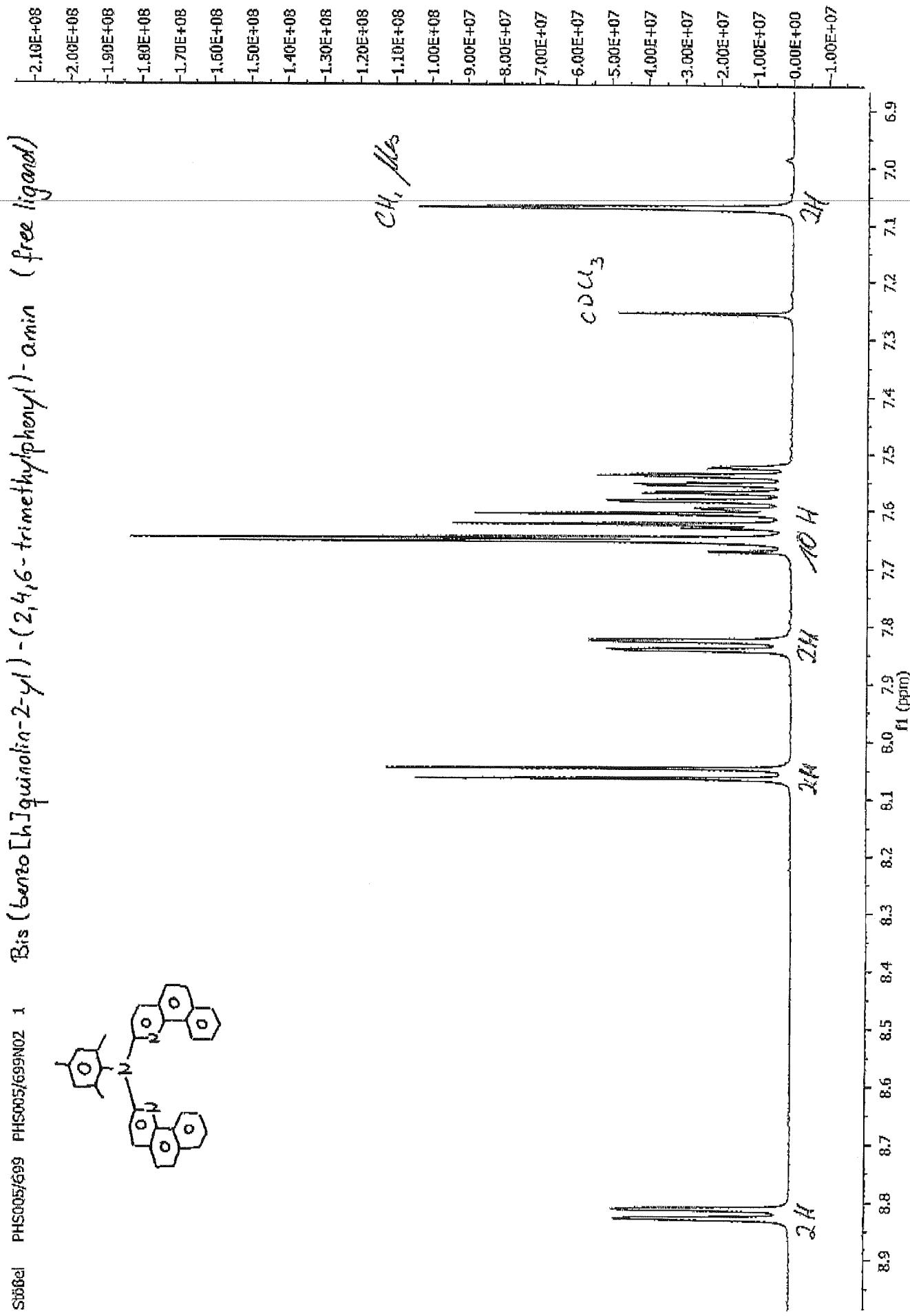
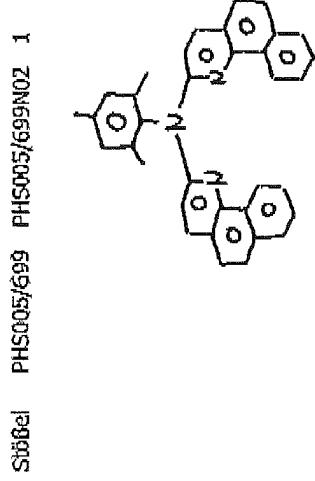
I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.



Dr. Philipp Stoessel

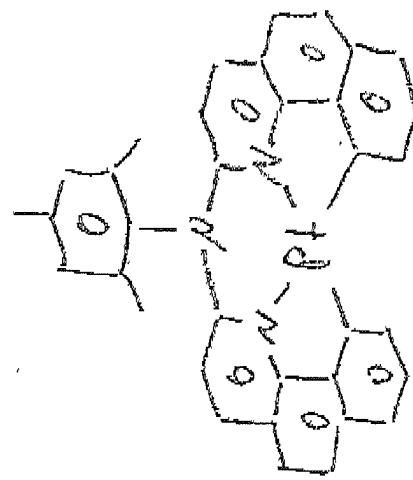
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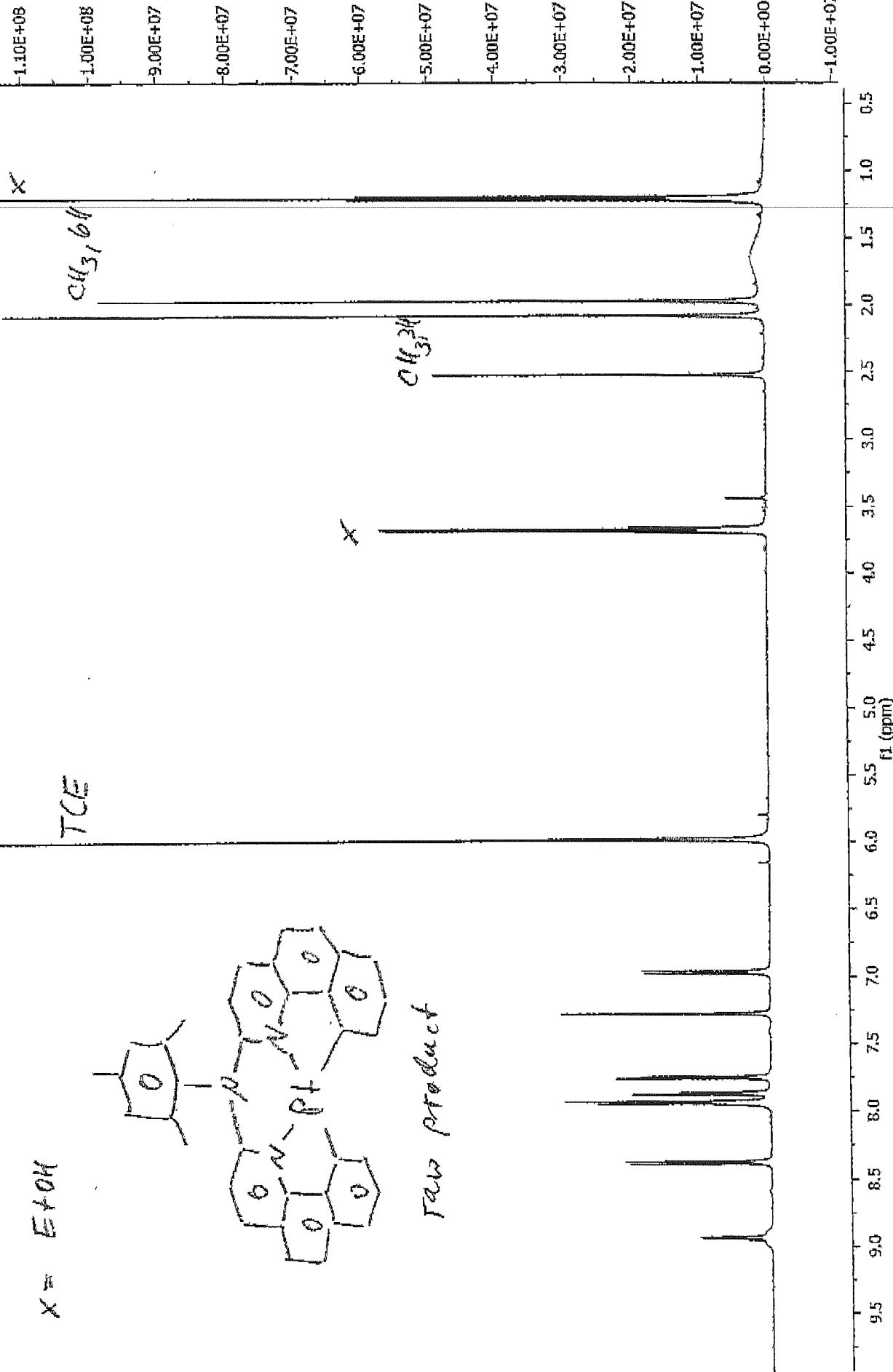


St00d PHS005/7/07 PH5005/7/07N02 1 Complex Pt-1

$\chi = E \cdot 10^4$

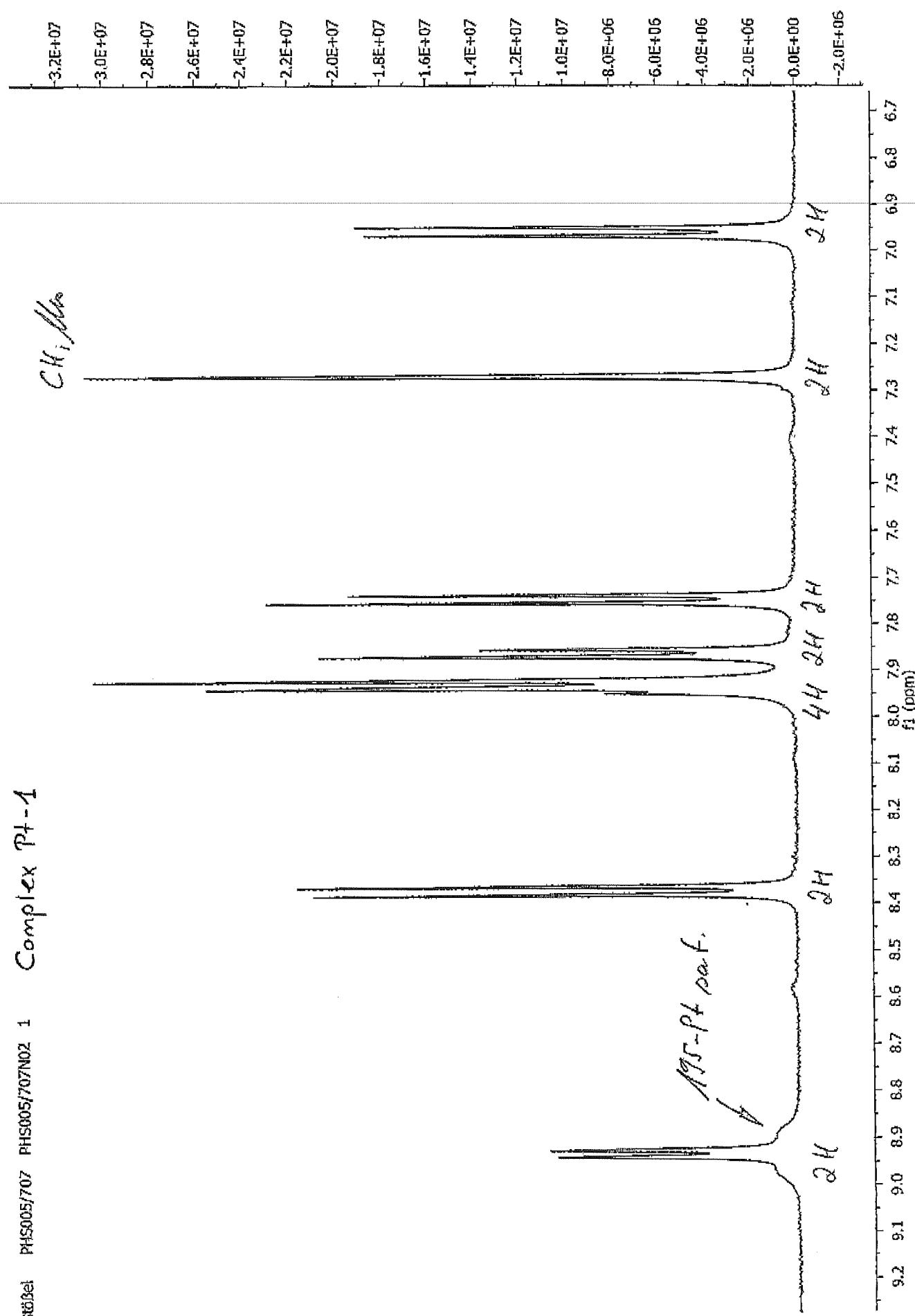


TCE



Stöber PHS005/707 PHS005/707N02 1 Complex Pt-1

CH₃/H₂O



PL film
Photoluminescence of complex Pt-1

